Kinetics of Neutrals and Ions in Cold Plasmas of H_2, H_2/D_2 and H_2/N_2 mixtures

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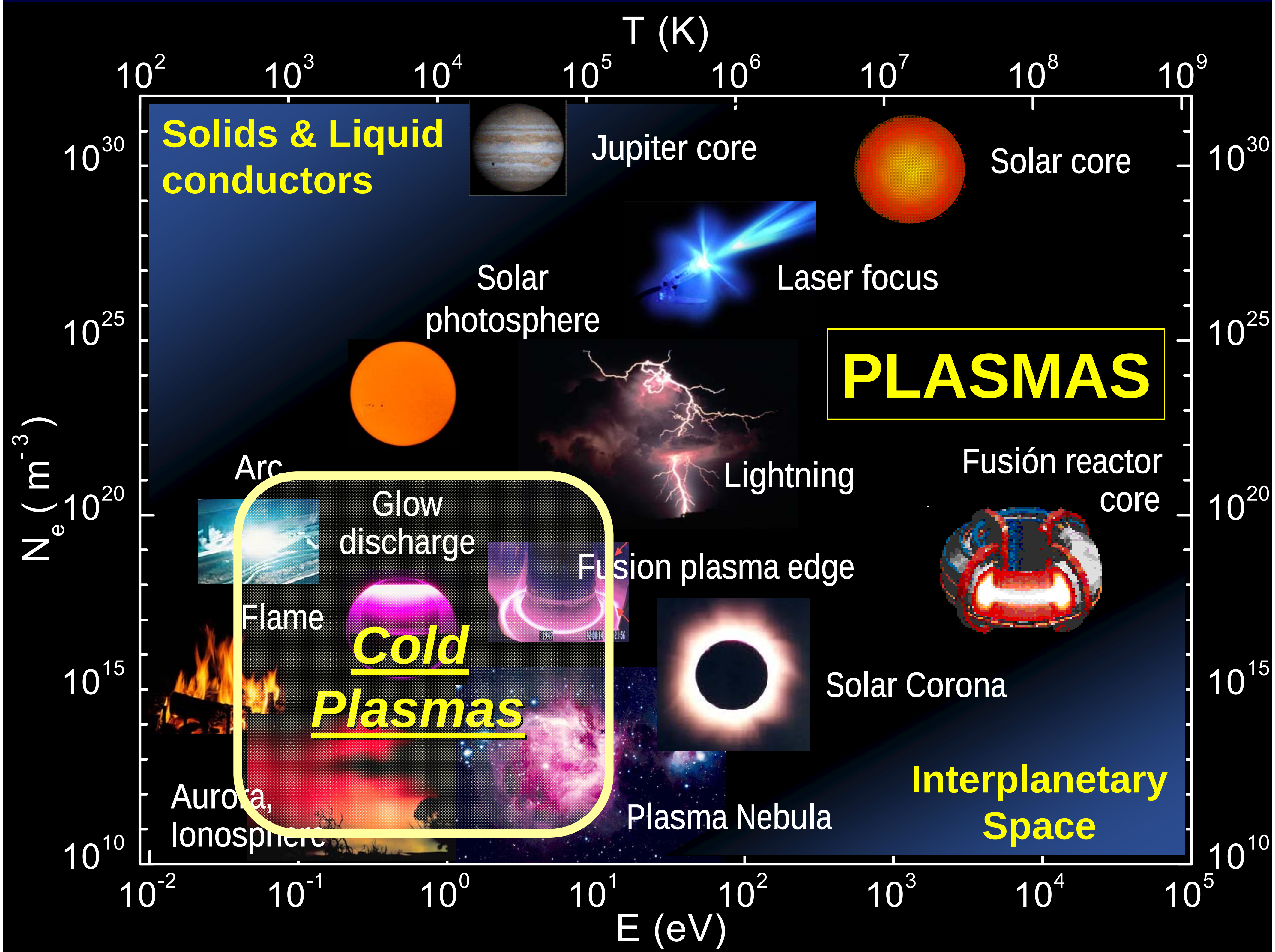


T (K)
10^2
10^3
10^4
10^5
10^6
10^7
10^8
10^9
Solids & Liquid conductors
Jupiter core
Solar core
Laser focus
Solar photosphere
PLASMAS
Arc
Lightning
Fusión reactor core
Glow discharge
Fusion plasma edge
Flame
Cold Plasmas
Solar Corona
Aurora, Ionosphere
Plasma Nebula
Interplanetary Space
N_e (m^-3)
10^30
10^25
10^20
10^15
10^10
E (eV)
10^-2
10^-1
10^0
10^1
10^2
10^3
10^4
10^5

"COLD" PLASMAS

Plasmas with Low Ionization Degree:

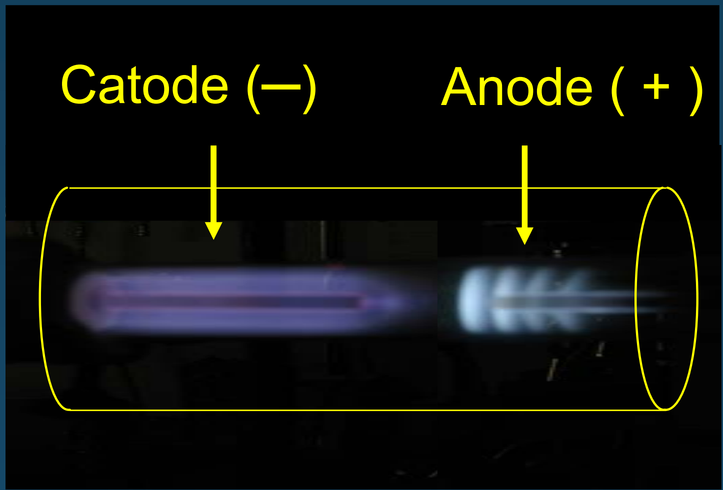
($N_e / N_{GAS} \sim 10^{-4}$-$10^{-6}$)

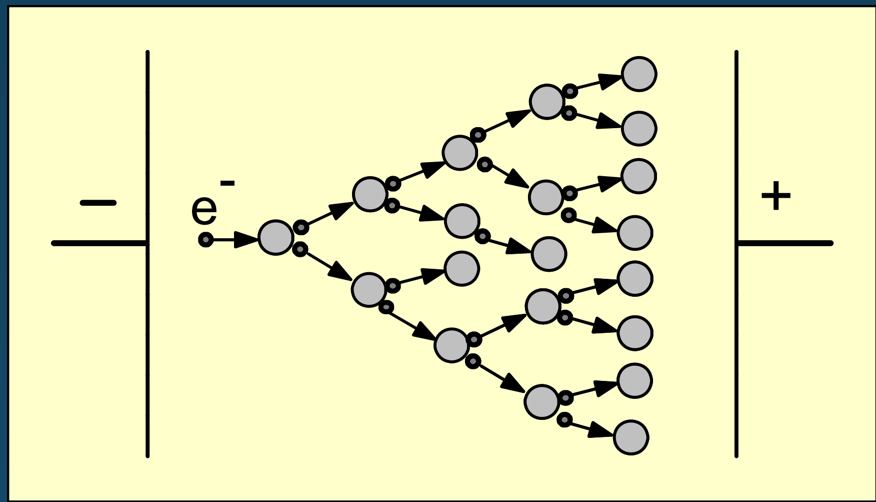
Far from Thermal Equilibrium:

High T_e ($\sim 10^4$-10^5 K) , Low T_{GAS} ($<10^3$ K)

Cold Plasmas in Laboratory :
Glow Discharges at Low Pressures

Free electrons gain energy from the electromagnetic field, ionize new atoms or molecules and establish the chain reaction.





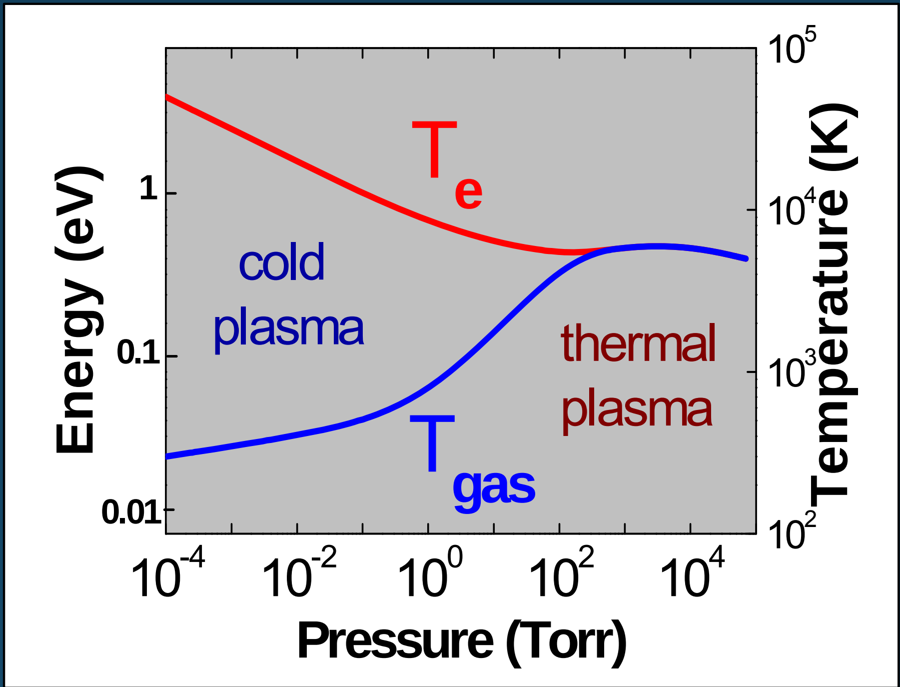
Stable discharges over a pressure range ~ 0.5 – 100 Pa (i.e.< 0.1 atm), determined by the suitable conditions for electron acceleration & multiplication in collisions with gas particles.

Example: Fluorescent Lamp

Why cold plasmas?

Elastic Collisions

Energy transfer from electrons to the heavier particles (neutrals and ions), Remarkably Inefficient !



$$E_{\max\ transmited} = \frac{4 m_e M}{(m_e + M)^2} E_{initial}$$

Energy transfer among electrons, Very Efficient ! (equal masses)

As pressure increases, the number of elastic collisions increases too and both temperatures get closer and equilibrates: thermal plasmas

Example of thermal plasmas: Arcs, Sparks

Electron Impact Processes

- Ionization $AB + e^- \rightarrow AB^+ + 2e^-$
- Dissociation $AB + e^- \rightarrow A + B + e^-$
- Excitation $AB + e^- \rightarrow AB^* + e^-$

Very reactive species are produced !

Secondary Processes

- Reactions in Gas Phase
- Heterogeneous Reactions

$\Rightarrow$ New Products

Very Reactive Media at "Room" Gas Temperatures !

- De-excitation of energy levels $\Rightarrow$ Light Emission !

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Interest of Cold Plasmas

Basic Research

- Identification and Study of Transient Species (Radicals, Ions)
- Spectroscopy of Transients and Excited States
- Interstellar Media Processes (Space Chemistry)
- Planetary Ionospheres (Earth, Titan, Giant Planets…)

Applied Research & Development

- Plasma-Assisted Thin Films Growth
- Plasma-Assisted Surface Processing
- Plasma-Wall interaction in Fusion Reactors

Issues of the Present Study

Cold Plasma Generation

Experimental Diagnostics

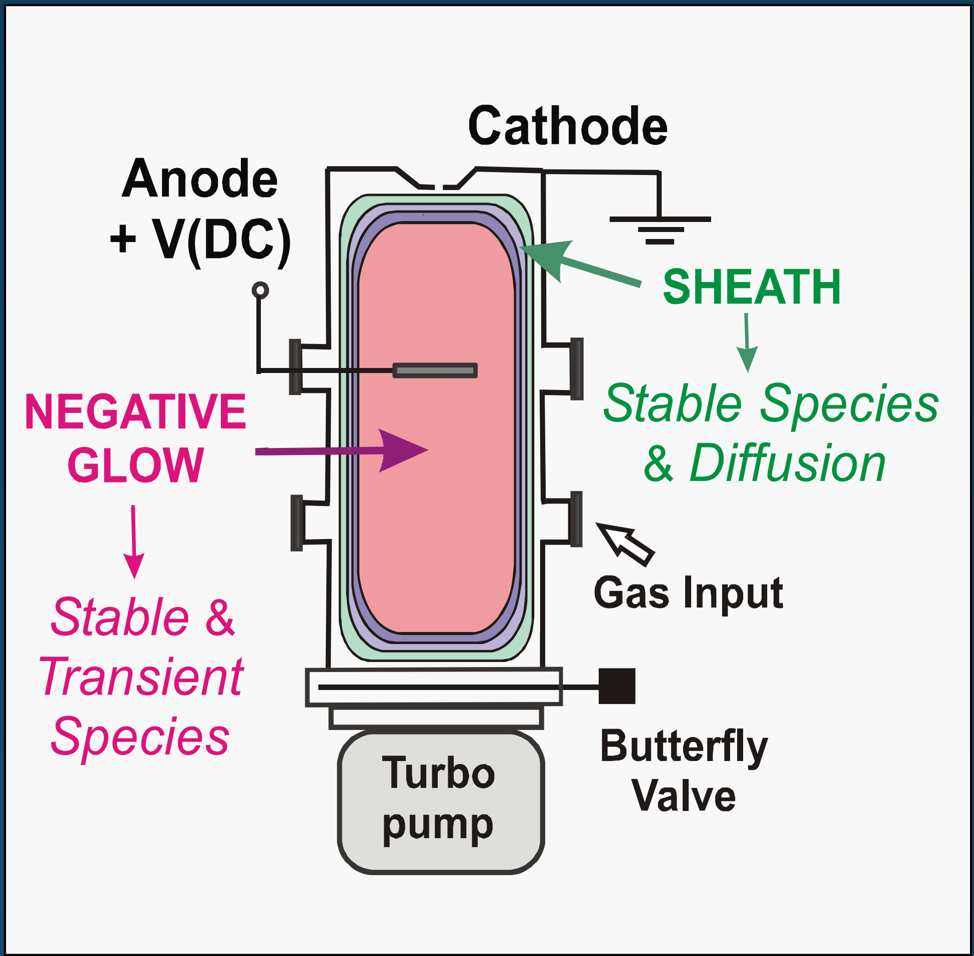
Kinetic Modeling

H_2	H_2/D_2	H_2/N_2

P ~ 0.8 – 8 Pa , i.e. (0.8 – 8)×10^{-5} atm.

Large changes of plasma properties with pressure have been observed !

Plasma Generation



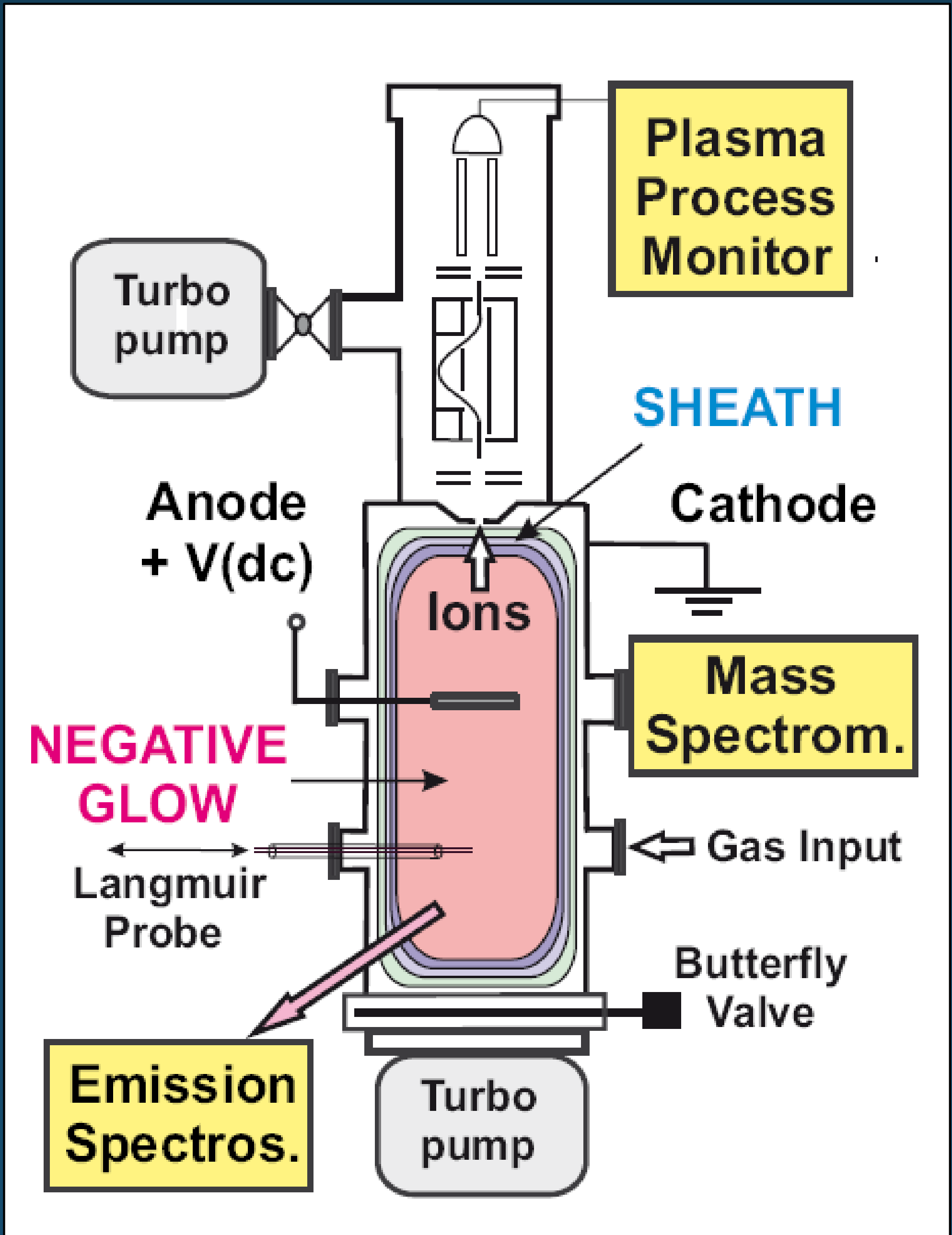
- Hollow cathode DC reactor
- Cathode: stainless steel vessel

E ≈ 0 in the Negative Glow !
Very stable & homogeneous plasmas at room temperature

Ions accelerate in the plasma sheath towards the cathode and neutralize in the wall.

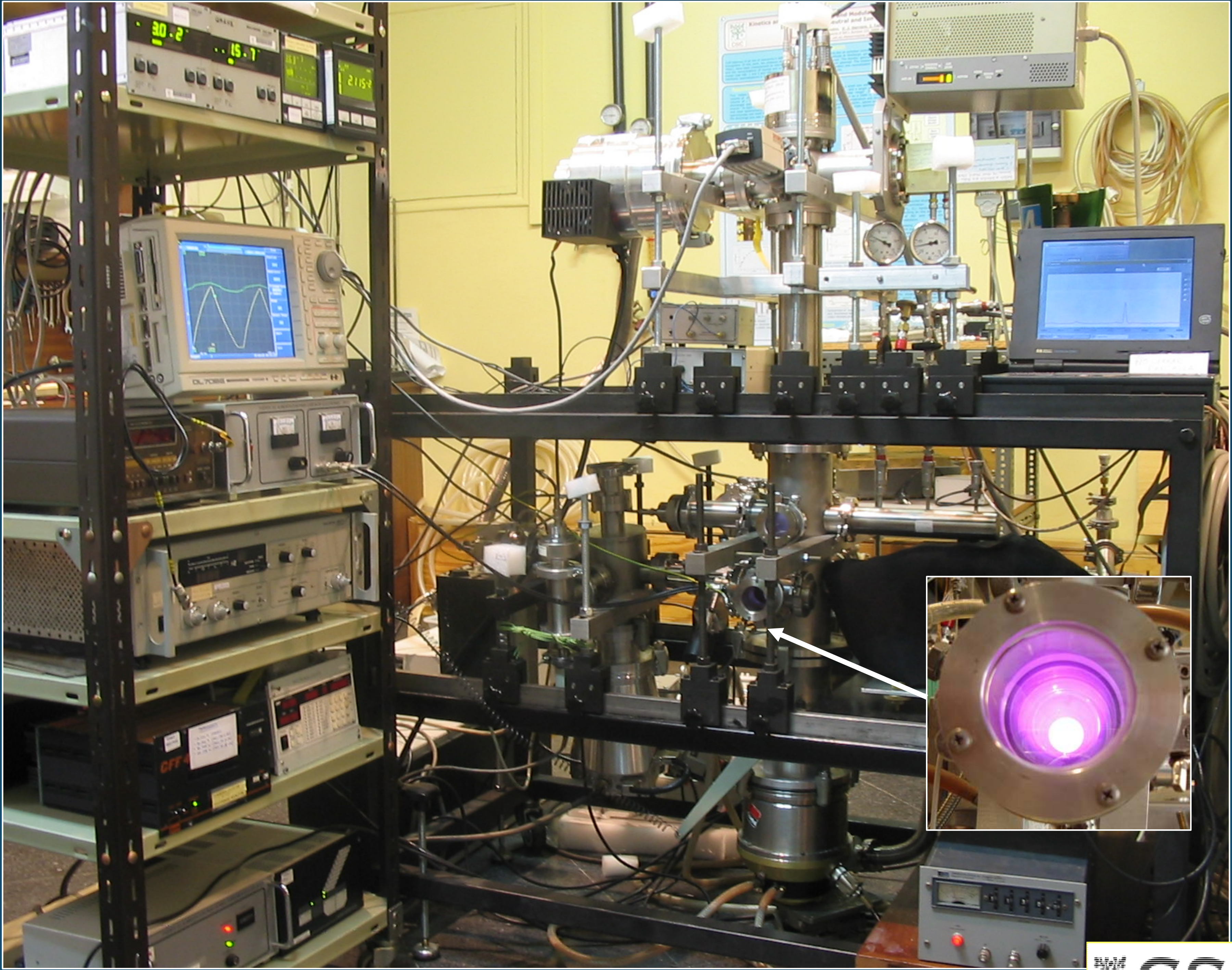
Neutrals diffuse and react in the wall.

Plasma Diagnostics



- Quadrupolar Mass Spectrometry of Neutrals (e^- impact ionization)
- Quadrupolar Mass Spectrometry of Ions + Ion Energy Distributions
- Double Langmuir Probes (N_e, T_e)
- Visible Emission Spectroscopy

  Excited States,
  Plasma Temperature,
  Relative H concentrations.



Cold Plasma Laboratory, IEM-CSIC

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Kinetic Models

"As simple as possible to understand the main mechanisms"

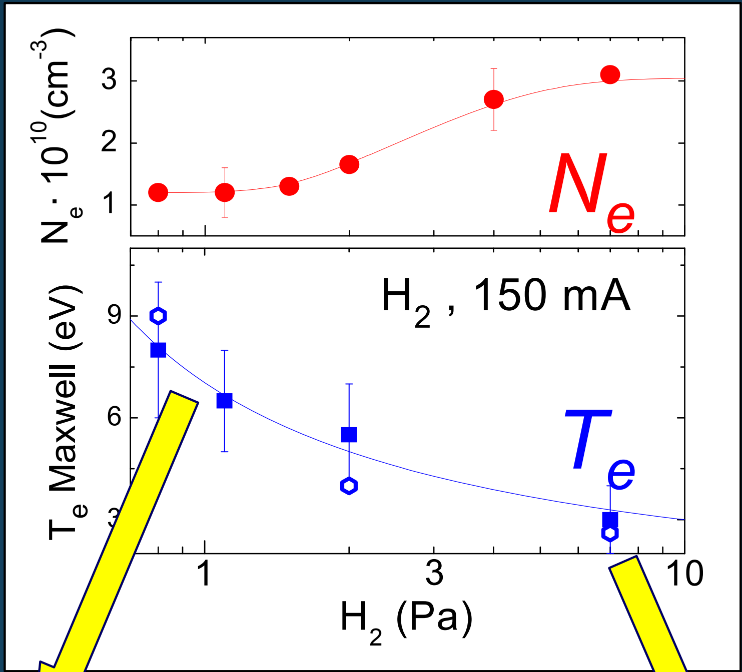
- Zero Order Models (2 volumes: Negative Glow and Plasma Sheath)
- A Time dependent Differential Equation for each Neutral and each Ion
- Maxwellian Electron temperatures

- Main Processes Considered
  - *Ionization + Dissociation by Electron Impact in the Glow*
  - *Bimolecular Reactions with No Potential Barrier ($k \neq f\,(T_{gas})$)*
  - *Diffusion through the Sheath*
  - *Heterogeneous Recombination and Neutralization*

- The Models do NOT include Three Body Reactions (Low Pressure)
- Neither Reactions with Potential Barrier (Low Gas Temperature)

H_2 Plasmas

H_2 Plasma Results



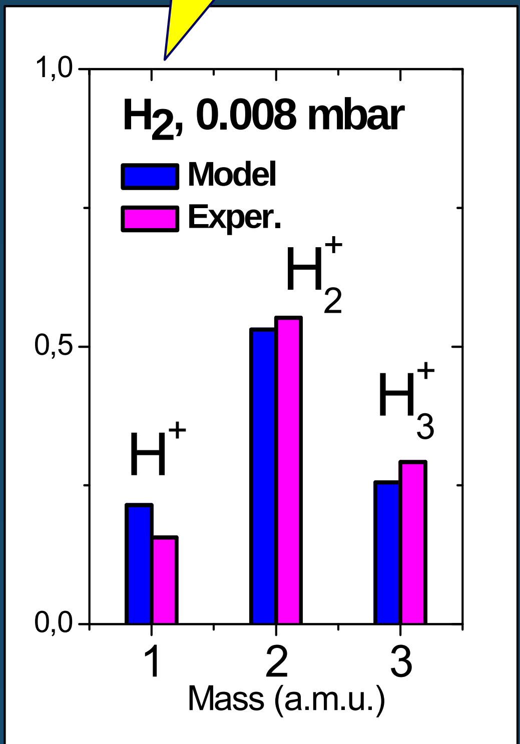
Ionization degree $N_e/N \approx 10^{-4}$

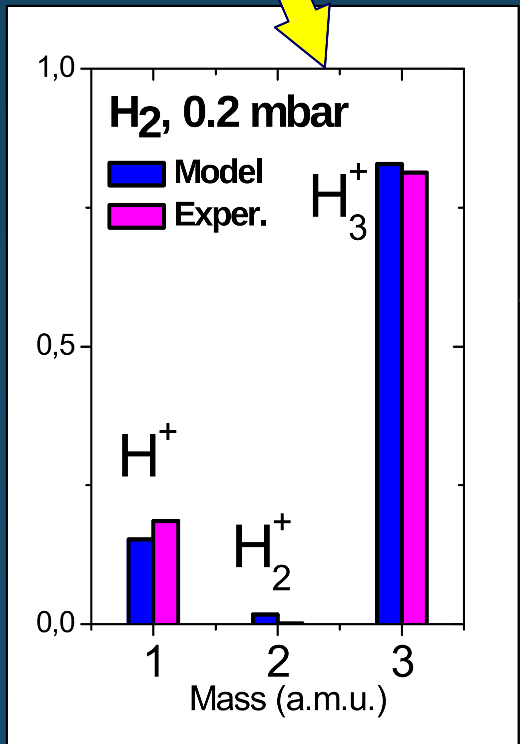
$T_e \approx 30.000 – 100.000$ K

$[H] / [H_2] \approx 0.10 – 0.15$

$T_{vib} (H_2) \approx 3.000$ K

$T_{rot} (H_2) \approx 300$ K $\approx T_{ion}$





Major Ion changes from

H_2^+ to H_3^+

with increasing pressure

Méndez, Gordillo, Herrero, Tanarro, J. Phys. Chem. A, 110, 6060 (2006)

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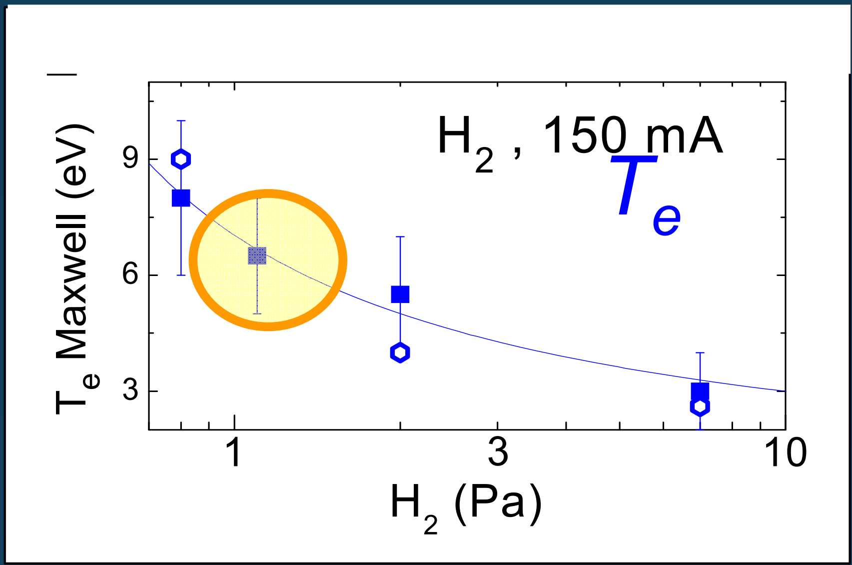
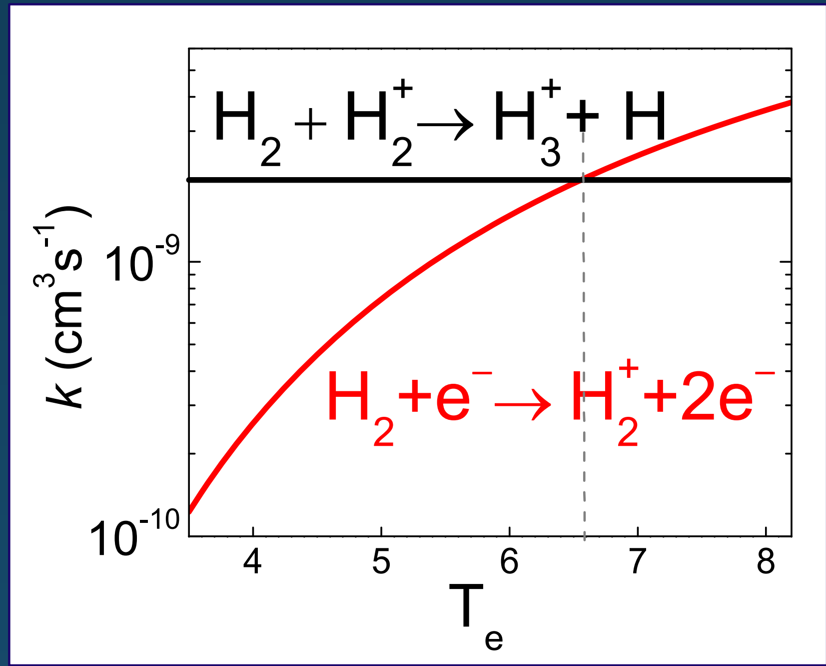
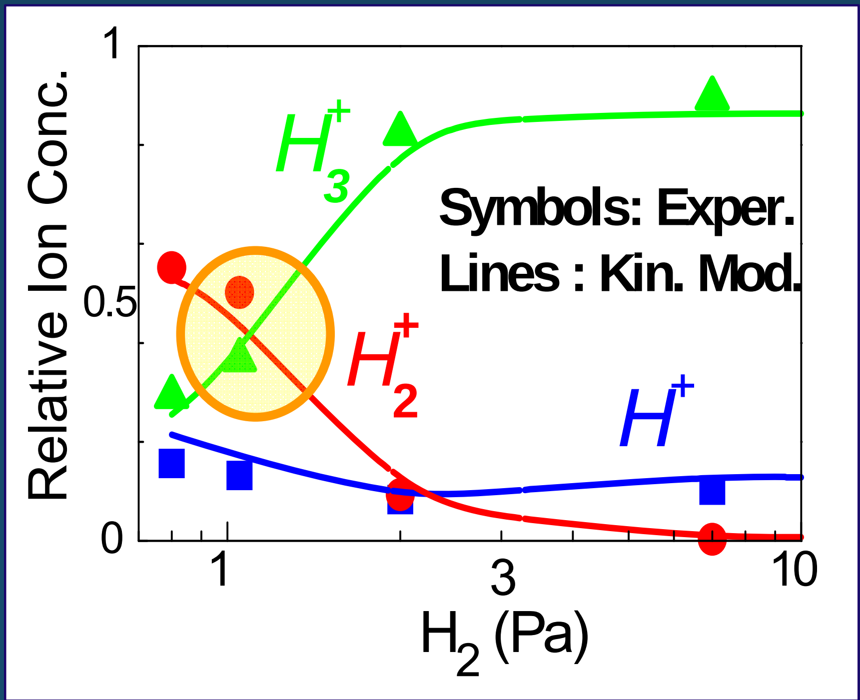
Inversion of Major Ion from H_2^+ to H_3^+ ?







Balance

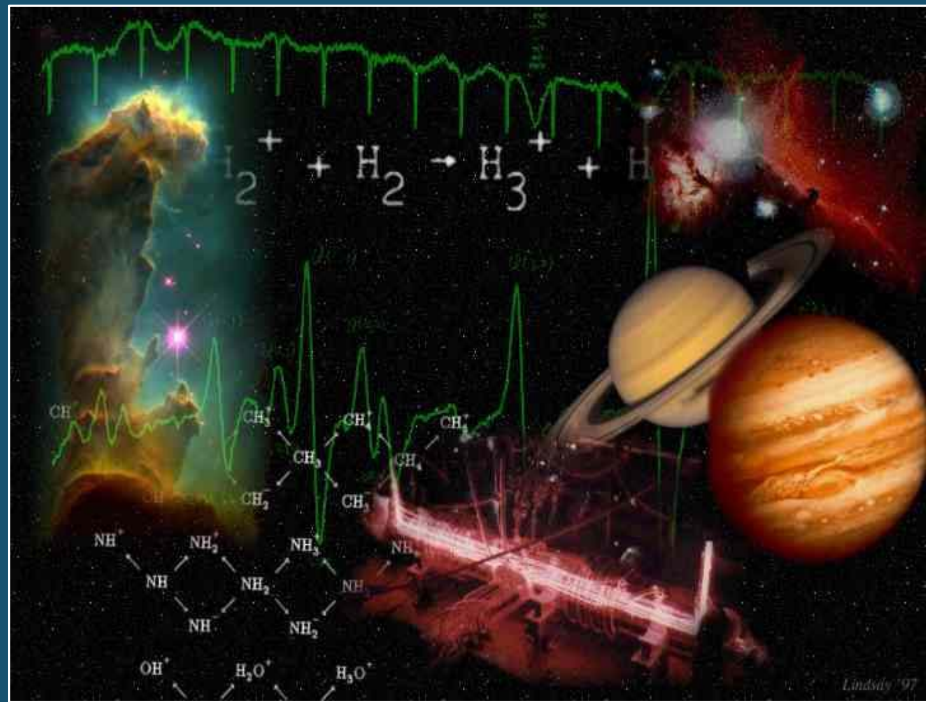
e^- Ionization ⇔ $H_2^+ + H_2$ Reaction

Satisfactory agreement experiment-model

H_3^+ *Key Ion in Space & Ionospheres of Jupiter & Gigant Planets*

H_3^+ Formation in Space:

1. H_2 + Cosmic Ray $\rightarrow H_2^+ + e^-$
2. $H_2^+ + H_2 \rightarrow H_3^+ + H$



H_3^+ : essential in the formation of water and other molecules in space at very cold temperatures, through barrierless reactions.

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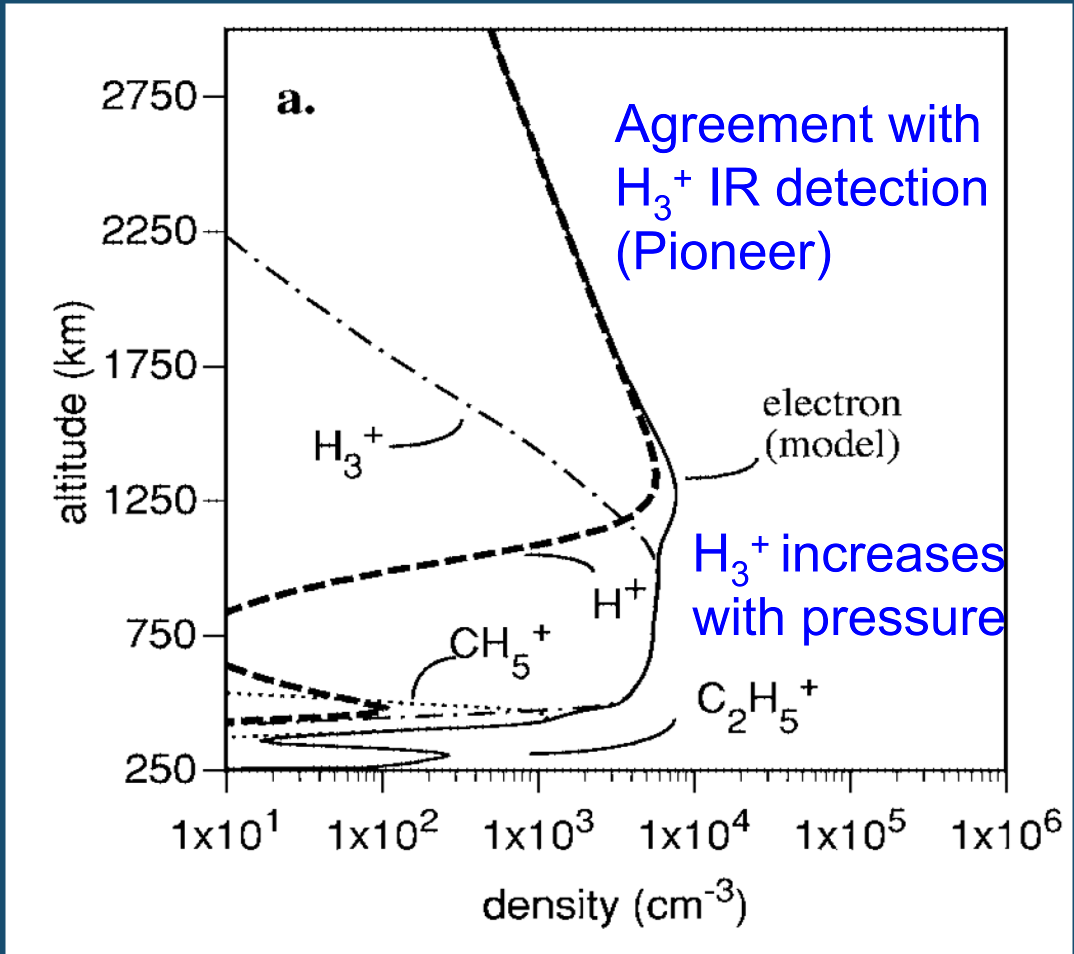
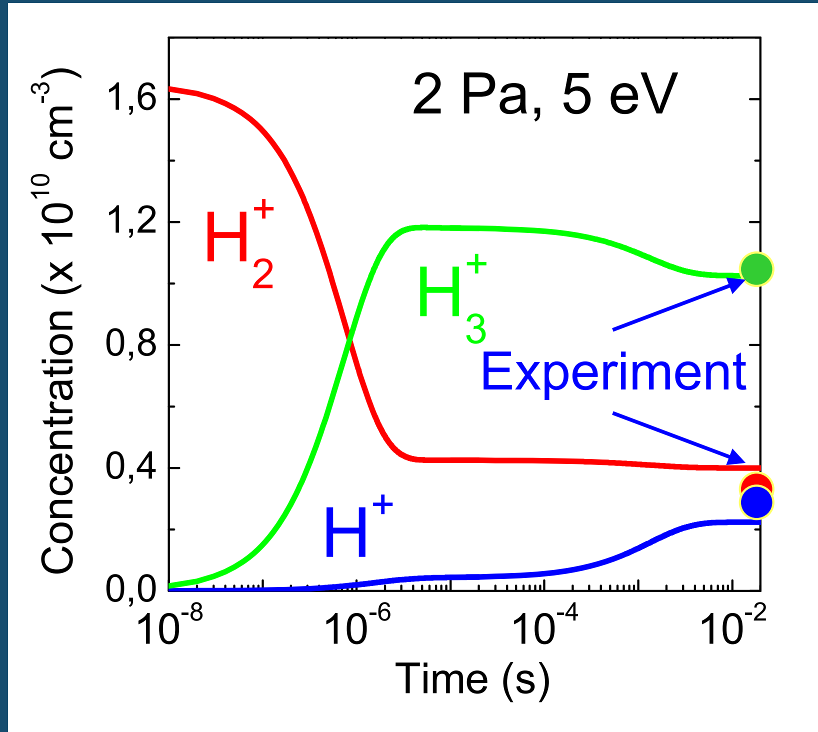
Jupiter Ionosphere



- P ~ Pa
- Characteristic Height ~ 1000 km
- Characteristic Time ~ 100 - 1000 years

Plasma Reactor



Tanarro, Herrero, Plasma Sources Sci. Technol. 20, 021006 (2011)

- P ~ Pa
- Characteristic Length ~10 cm
- Characteristic Time < 0.01 s

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Neutrals in H_2 discharges: H & H_2

$[H] / [H_2] \approx 0.10 – 0.15$

Why so high concentration of H, a transient species?

$H_2 + e \xrightarrow[k\,(T_e)]{} 2\,H + e$

$2\,H + \text{wall} \xrightarrow[\gamma_{Ads.} + \gamma_{Rec.}]{} H_2$

Balance

(not three body reactions at low pressure)

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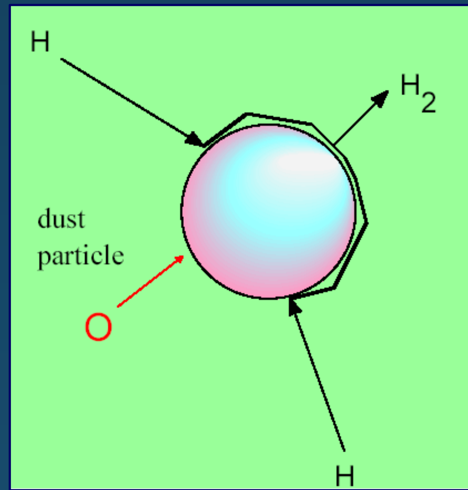
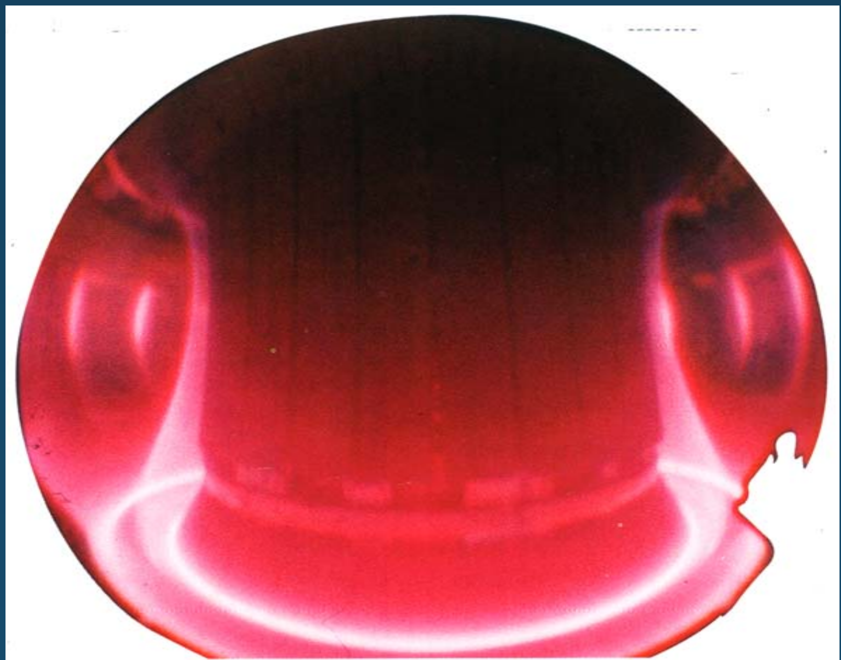
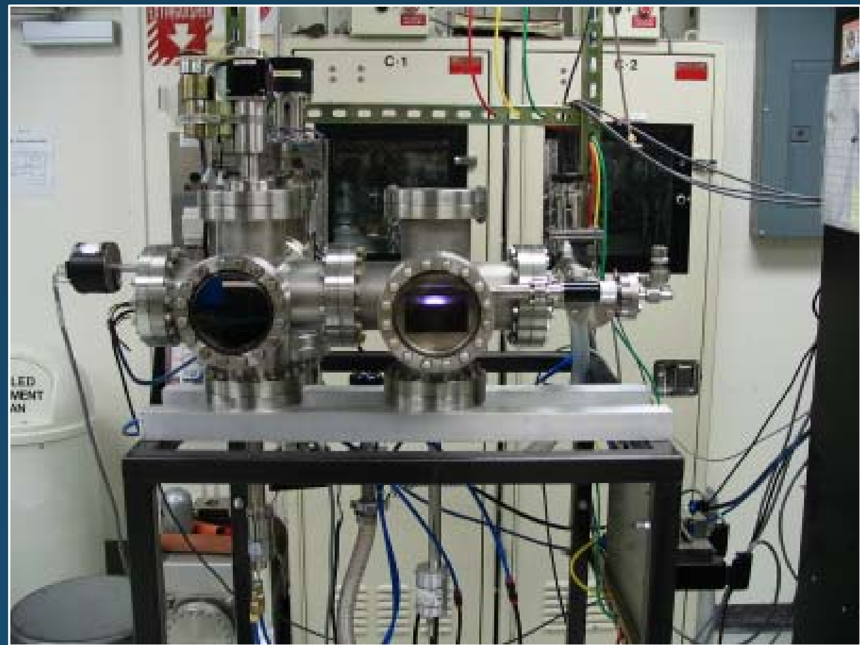
H_2 concentrations unexpectedly large in interstellar space!
H_2 formation on dust surfaces!



- *Interest in Fuel Recycling from the walls in Experimental Fusion Reactors (D + T).*
- *Interest in Thin Film Growth of H rich compounds...*





Unfortunately, in pure H_2 discharges, the H_2 precursor, renewed continuously by the gas flow, can't be distinguished from the H_2 produced in the surfaces !!!

H_2+D_2 plasmas would help to clarify the relevance of the heterogeneous processes, and also, the isotopic exchange chemistry!

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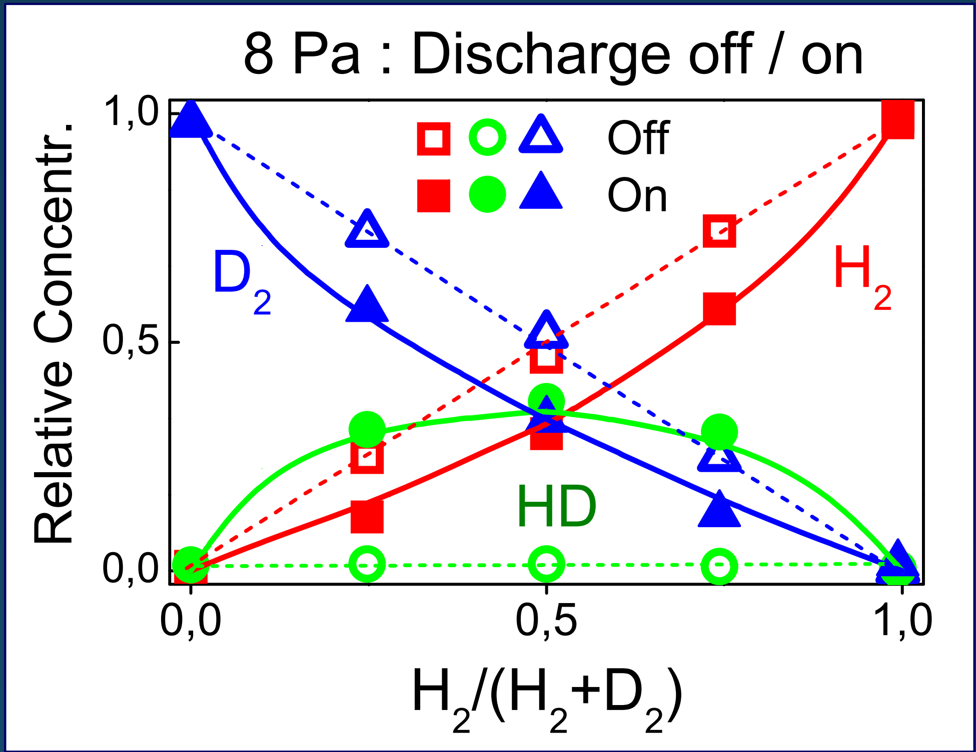
$H_2 + D_2$ Plasmas

$H_2 + D_2$ Plasma Results



NEUTRALS

- HD is generated in the wall
- H_2 & D_2 : precursors are also generated in the wall after dissociation of H_2 & D_2

H_2 / D_2 / HD Concentrations Balance :

Dissociation vs. *Surface Generation* vs. *Gas Flow Input & Exit*

The three species can be distinguished by mass spectrometry

Possible Surface Processes in H_2 + D_2 Plasmas

Langmuir-Hinshelwood : two adsorbed atoms reacts and desorb.

Example: $H(s) + D(s) \rightarrow HD$

a) Relevant in the Space, for physisorbed atoms on the surface of dust grains.

b) Relevant in catalysis.

c) Needs an "activation energy" (E(reaction) + E(desorption))

Eley-Rideal : an incident atom reacts with an adsorbed one.

Example: $H + D(S) \rightarrow HD$ (γ_H & γ_D : wall coefficients)

Most probable process in laboratory plasmas :

a) High fluxes of free atoms to the surfaces $\Rightarrow$ high coverage

b) Chemisorbed species on the wall material.

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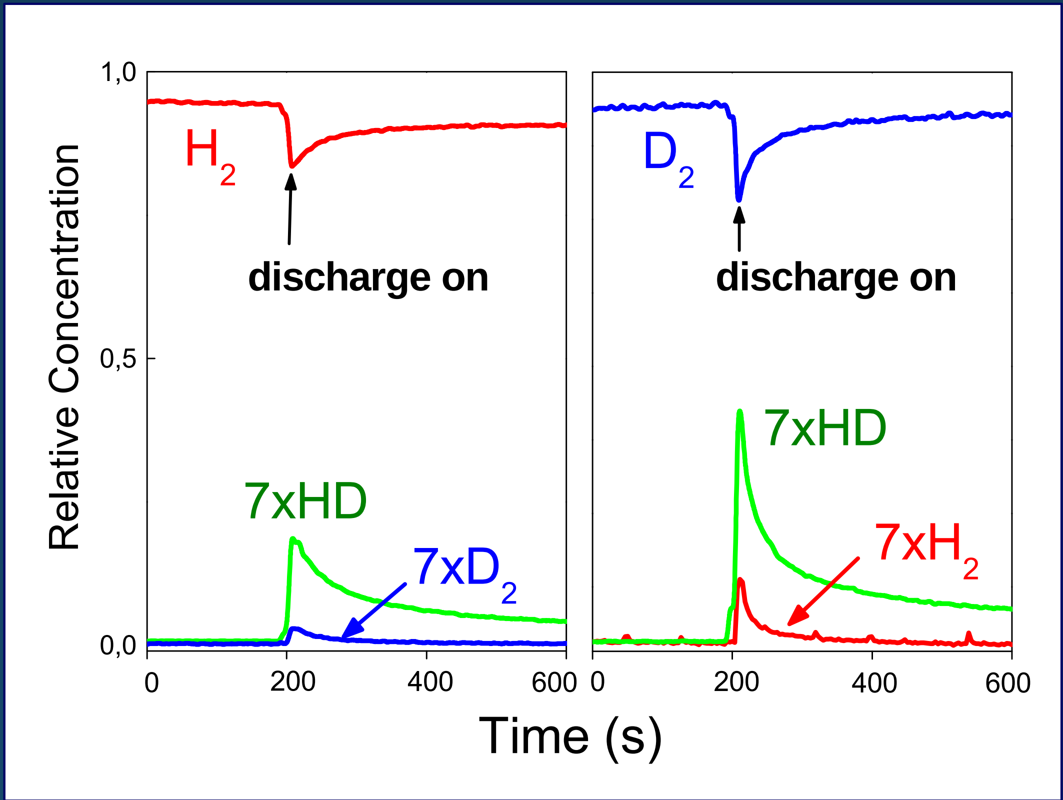
Hints of Eley-Rideal behaviour in our H_2+D_2 plasmas :



Time Resolved Experiment,
with H_2 or D_2 as pure precursor,
after "filling" the wall with
the other gas (D_2 or H_2)

$\Downarrow$

HD is generated more efficiently
by D impact on the H rich surface:

$$\boxed{\gamma_D > \gamma_H}$$

$\Downarrow$

Typical of ER : Longer interaction time for the incoming D with H(s),
D, being heavier, moves more slowly than H.

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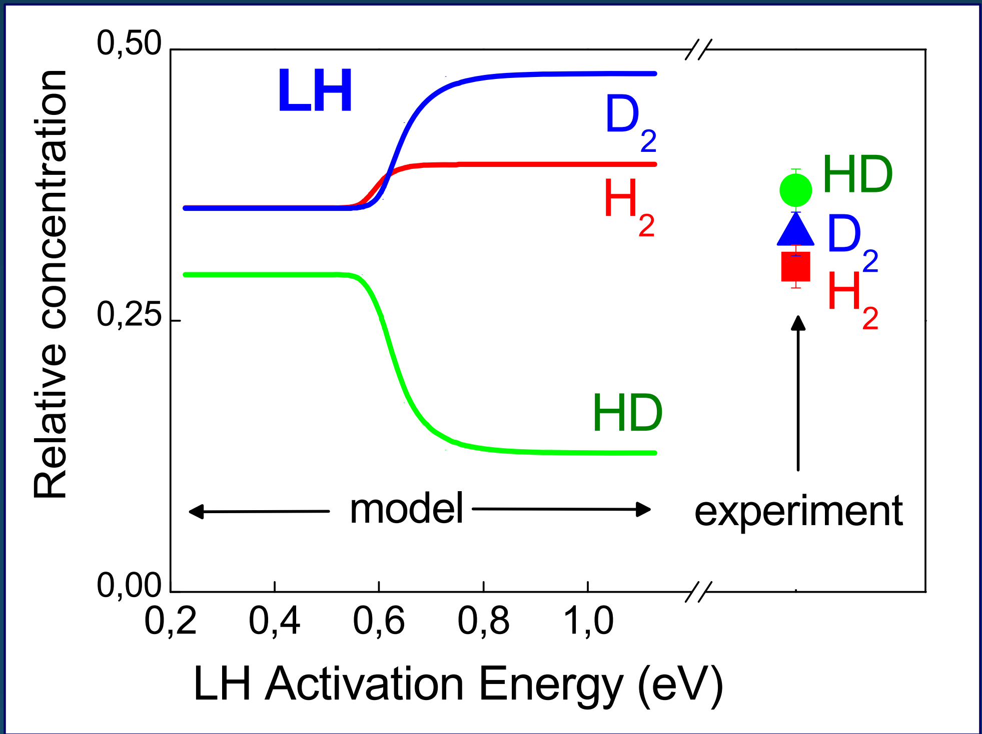
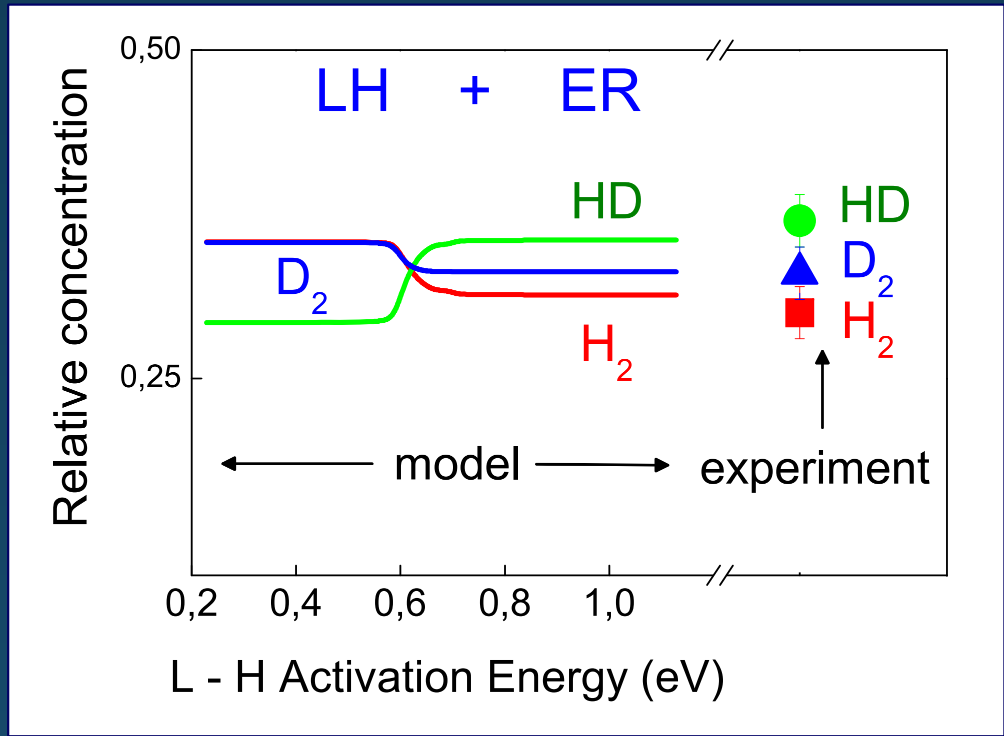
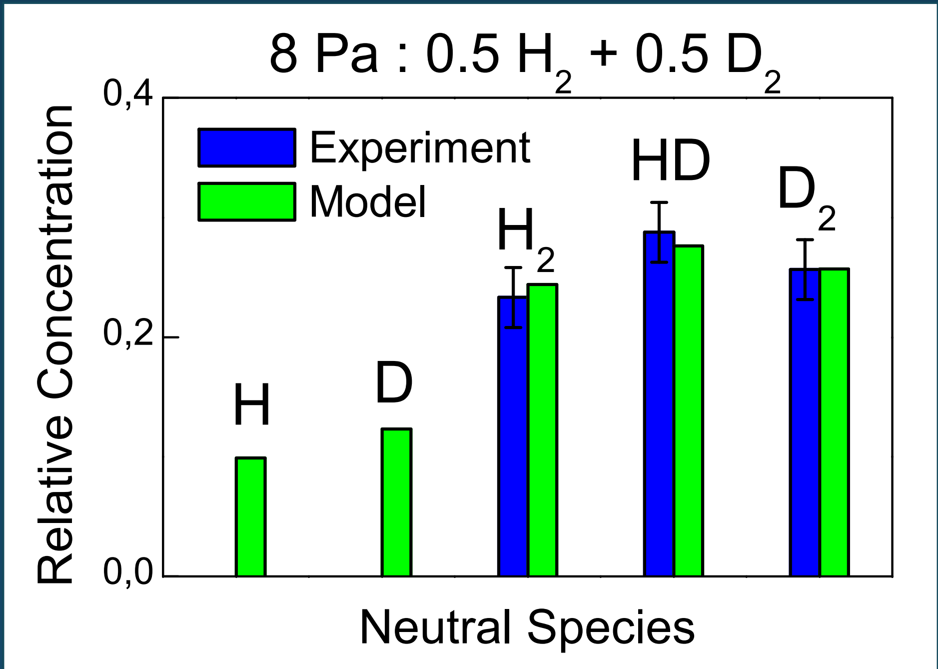
Disregarding the possible influence of the Langmuir-Hinshelwood process





- LH would be relevant only for activation energies below ≈ <u>0.6 eV</u>.
- At higher energies, LH does not interfere with the ER process
- ER is the origin of HD formation in our plasmas !

By comparing Model / Experiment $\Rightarrow$ Eley-Rideal γ values :



- $H + D(S) \rightarrow HD$, $H + H(S) \rightarrow H_2$

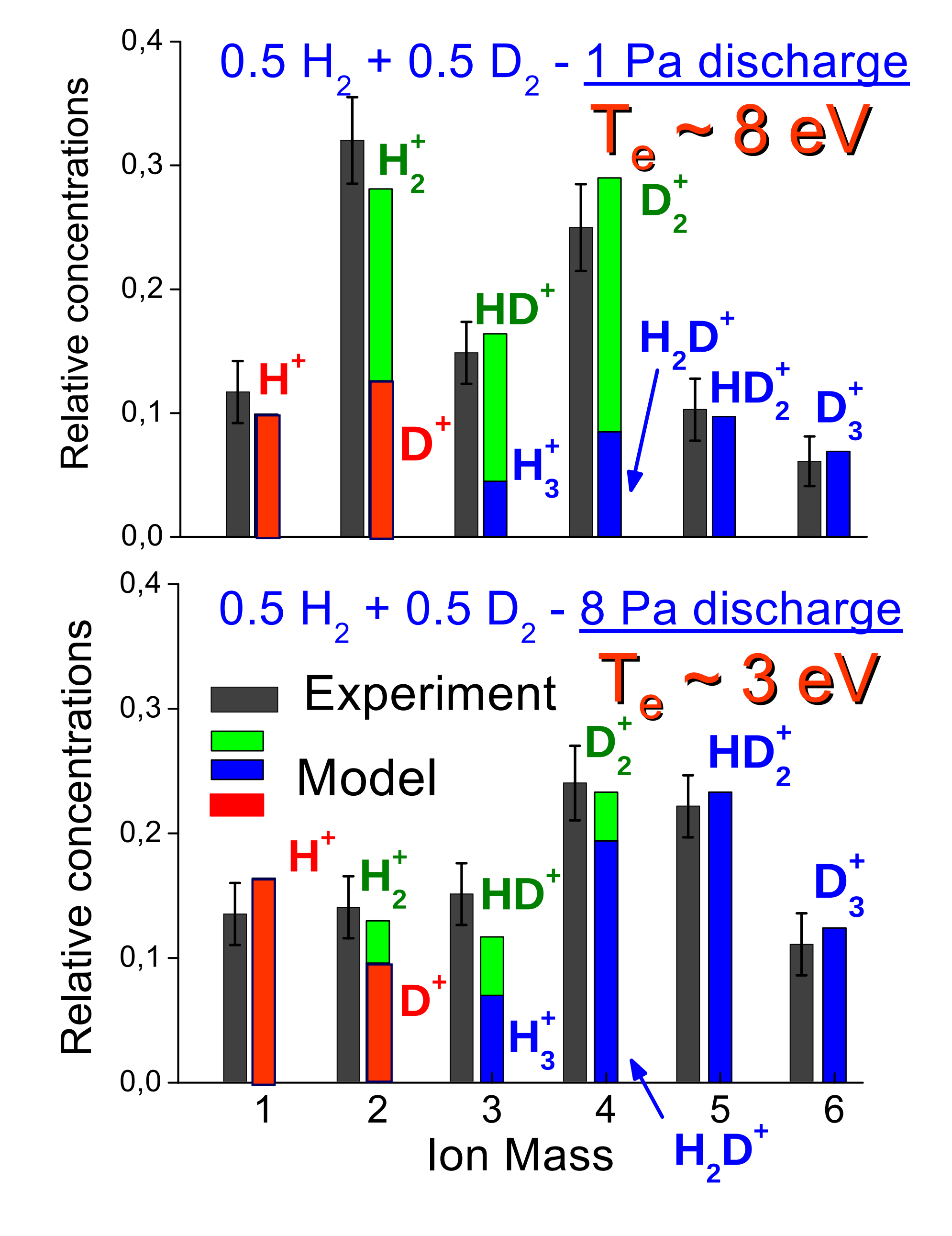
$$\boxed{\gamma_H = 0.0015}$$

- $D + H(S) \rightarrow HD$, $D + D(S) \rightarrow D_2$

$$\boxed{\gamma_D = 0.0020}$$

Jiménez-Redondo, Carrasco, Herrero, Tanarro, PCCP, 13, 9655 (2011)

The model fits very well the experimental data.
The model allows to estimate also the concentrations of H & D atoms.



H_2+D_2 , IONS

Ion-Molecule Reactions :

<u>Isotopic variants of</u> : <u>Nº reactions</u>:

- $H_2^+ + D \rightarrow H_2 + D^+$ (6)
- $H^+ + D_2 \rightarrow D^+ + HD$ (4)
- $H_2^+ + D_2 \rightarrow H_2D^+ + H$ (16)
- $H_3^+ + D_2 \rightarrow H_2D^+ + HD$ (15)

<u>Complete model ~ 70 reactions</u>

Triatomic ion concentrations increase with decreasing T_e, like in pure H_2.

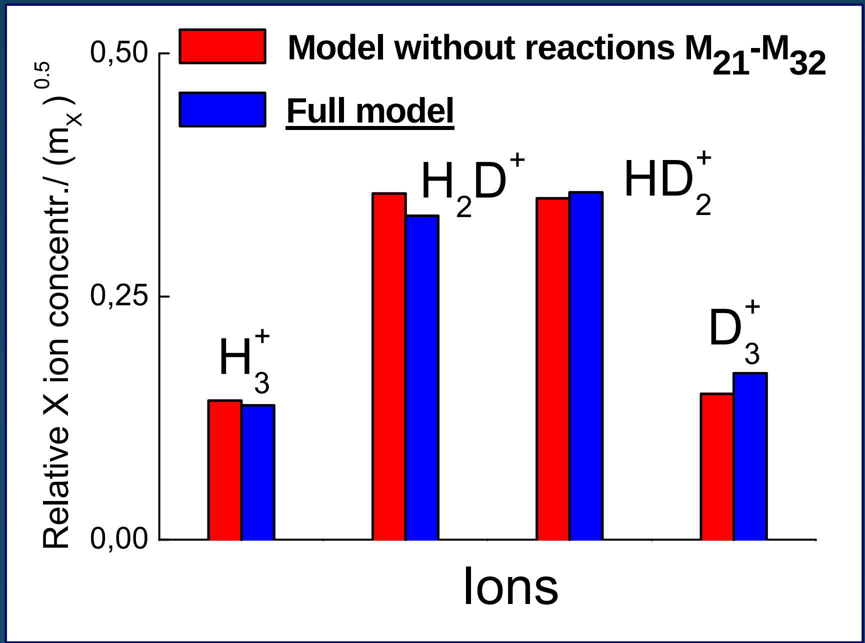
Balance : Direct Ionization $\Leftrightarrow$ Ion-molecule reactions

Influence of some groups of reactions of interest in Astrophysics

Model with / without reactions type:

$H_3^+ + D_2 \rightarrow H_2D^+ + HD$

(triatomic ions' reactions)

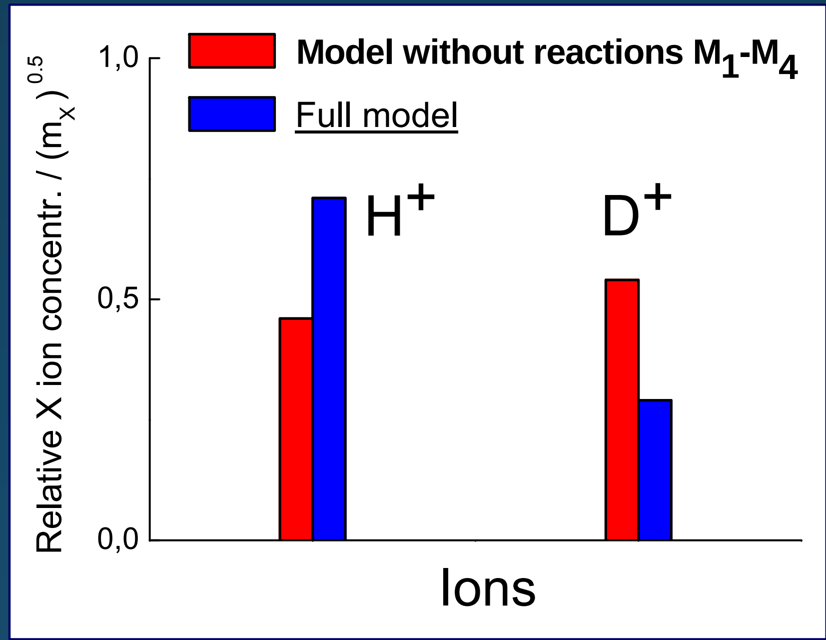


Small effect of these reactions. Important at lower temperatures.

Model with / without reactions type:

$H^+ + D_2 \rightarrow D^+ + HD$

(monoatomic ions' reactions)



Zero point energy effect noticeable even at room gas temperatures !

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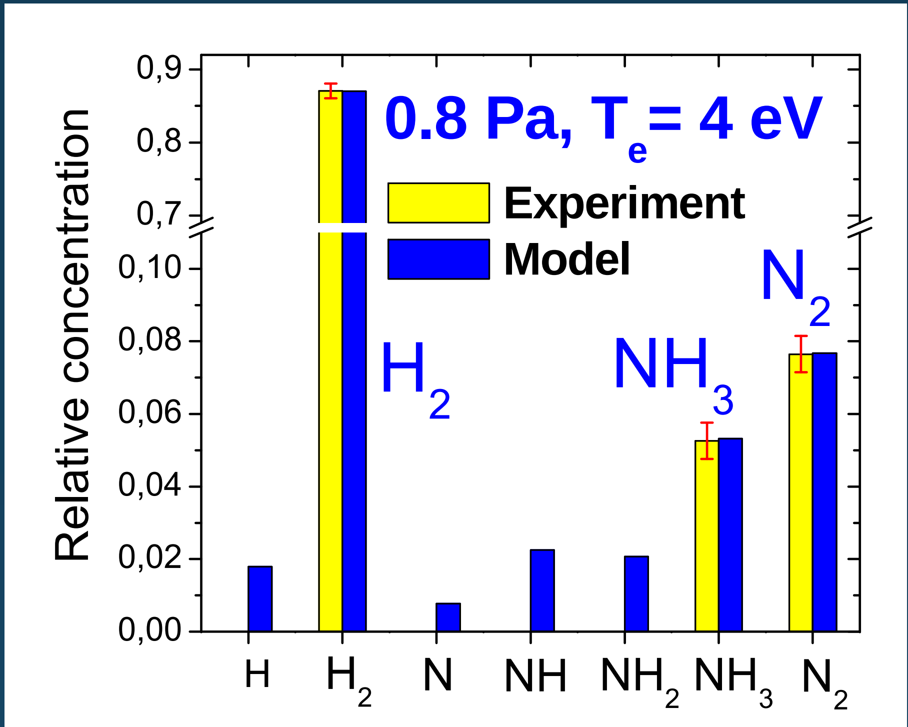
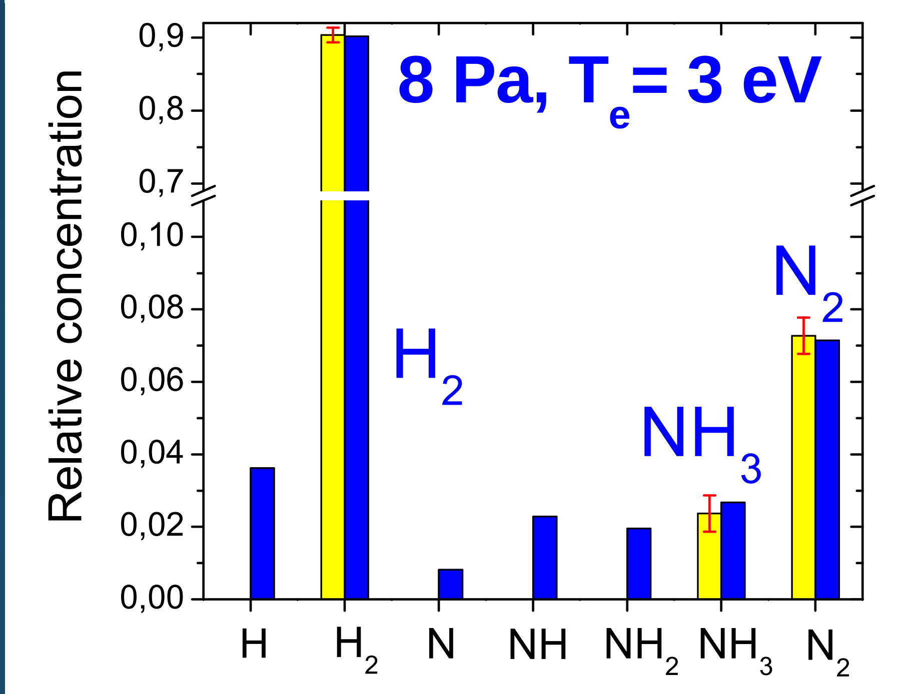
$H_2 + 10\% \; N_2$

H_2 + 10% N_2 results





NEUTRALS

NH_3 formation by wall reactions involving H, NH & NH_2 transients.

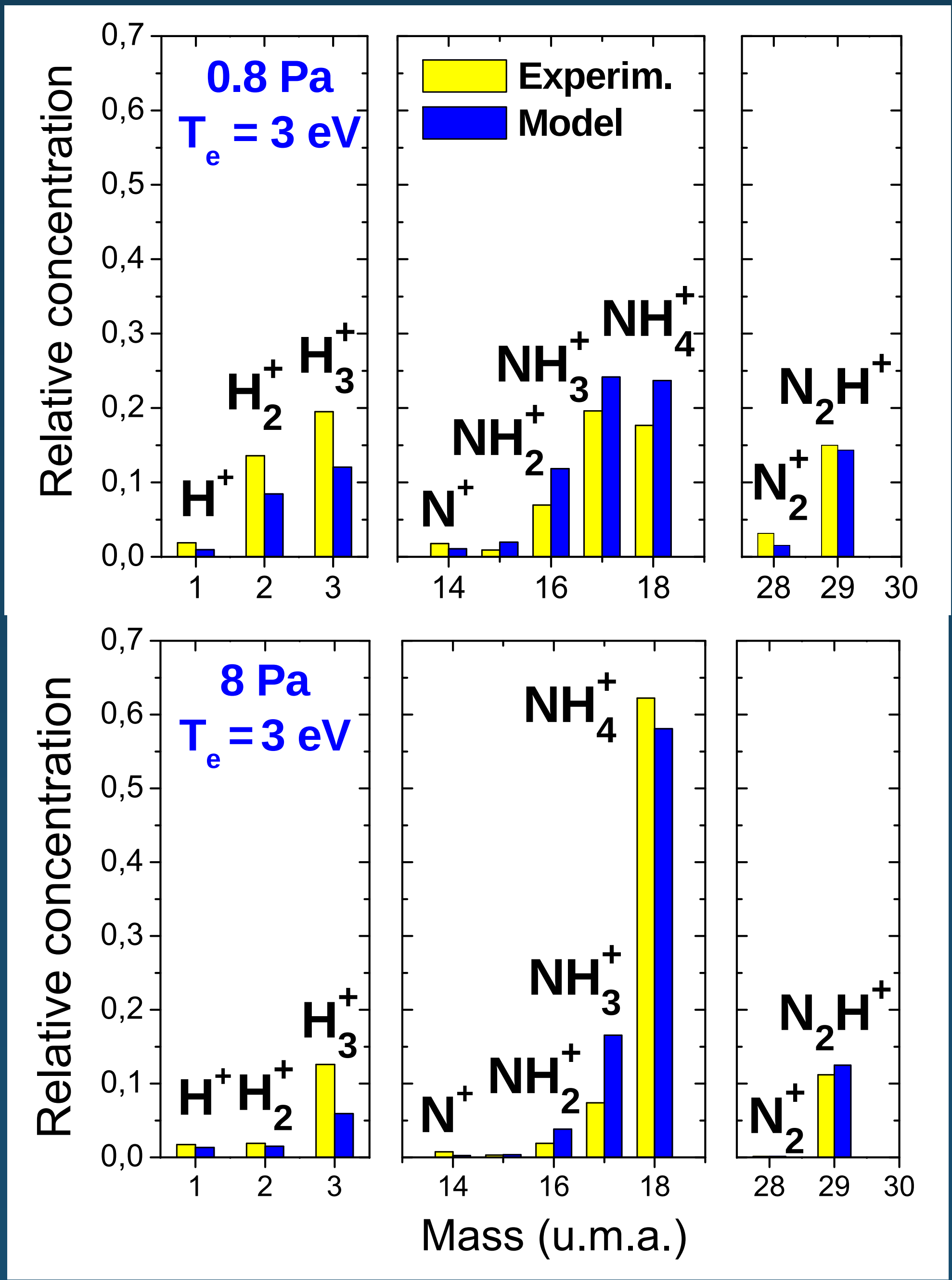
E-R & L-H processes necessary.

Balance :

- *e^- Impact Dissociation*
- *Surface formation*
- *Gas flow input / exit.*

At higher P $\Rightarrow$ lower T_e :
H_2 & N_2 dissociations decrease, and NH_3 concentration goes down.

$H_2 + 10\%\ N_2$ results



IONS

Large variations of Ion Concentrations with small pressure increase.
Prevalence of protonated ions over the parent ones, specially NH_4^+, which does not react in gas phase, at the higher pressure (lower T_e).

Main Ion-Molecule Reactions

$N_2 + H_2^+ \rightarrow N_2H^+ + H$
$N_2 + H_3^+ \rightarrow N_2H^+ + H_2$
$H_2 + N_2^+ \rightarrow N_2H^+ + H$
$NH_3 + H_2^+ \rightarrow NH_3^+ + H_2$
$NH_3 + H_3^+ \rightarrow NH_4^+ + H_2$
$NH_3 + N_2H^+ \rightarrow NH_4^+ + N_2$

$k \geq (2\text{–}6) \times 10^{-9}$ $cm^{-3}\ s^{-1}$

(Complete model ~ 80 reactions)

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Interest of N_2H^+ formation in the Space:

$$H_3^+ + N_2 \rightarrow N_2H^+ + H_2$$

Nitrogen is the 5th Most Abundant Element in the Universe

but N_2 does not have observable Vib - Rotational transitions

The Infrared Spectra of N_2H^+

allows to estimate the N_2 abundance in dark clouds

Possible interference of NH_3 in the N_2/NH_2^+ balance.

NH_3 can lead to NH_4^+ formation, still undetected (but predicted) in Space .

SUMMARY & CONCLUSIONS

- H_2, H_2+D_2 & H_2+ N plasmas studied experimental and theoretically.
- Large changes were found in their T_e & Neutral & Ion concentrations with pressure (P ~ 0.8 – 8 Pa).
- The kinetic models developed allow to identify the main processes responsible of the observed behavior in each case, and fit quite encouragingly the large set of experimental data.

- *Dependence of $k_{Dissoc.}$ and $k_{Ioniz.}$ with electron temperature.*
- *Relevance of ion-molecule barrierless reactions.*

  H_3^+, N_2H^+, NH_4^+ tend to be prevalent at low T_e in H_2 dominated plasmas.
- *Relevance of surface reactions: LH vs ER processes*

  Efficient formation of HD, NH_3 and regeneration of the precursors H_2, D_2 and N_2, previously dissociated.

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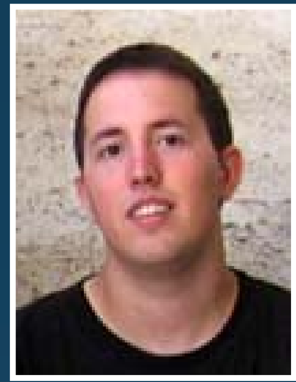
The Team

Myself

Prof. Víctor J. Herrero

Dr. Esther Carrasco
PhD Contract



Miguel Jiménez
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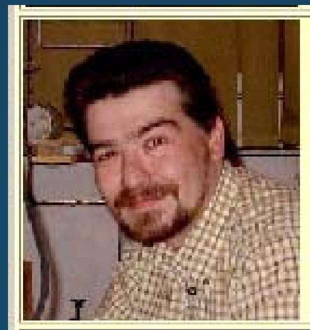
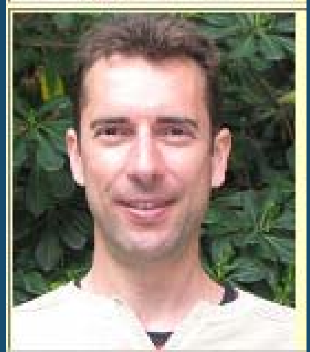
The Excellent Technicians of our Department

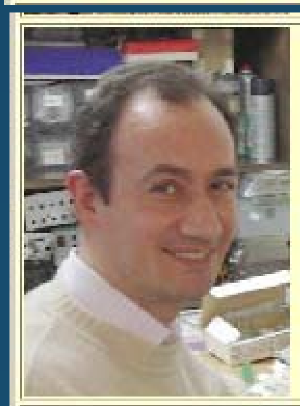
Mª José Malagón



Miguel A. Moreno



David Pérez



Javier Rodríguez

Thank you very much for your attention !

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